

✂ Estimation of Supercritical Fluid-Liquid Solubility Parameter Differences for Vegetable Oils and Other Liquids From Data Taken with a Stirred Autoclave

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Fujishiro and Hildebrand developed a procedure for determining the solubility parameter difference between the components of a partially miscible binary mixture, knowing the molar volumes of the components and the composition of each phase. Using this procedure, the solubility parameter differences between supercritical carbon dioxide (SCCO₂) and each of three vegetable oils and four hydrogen bonding liquids have been determined. For the vegetable oils the solubility parameter differences at 72 C over the pressure range 5,000–10,000 psi were low, of the order of 2.0, and decreased only slightly with increasing pressure. For the hydrogen-bonding liquids at 52 C, over the same pressure range, the solubility parameter differences were much larger, of the order of 4 to 7 units, and independent of pressure except for ethylene glycol for which the difference increased from 5.7 to 6.7 from 5,000 to 10,000 psi.

There is much activity and interest today in SCF (supercritical fluid) technology both for extraction and SCF chromatography. In both applications it is desirable to have theoretical guidance to explain the effectiveness of separations and to provide predictive capability. Solubility parameters based on regular solution theory have proved very useful in a variety of situations (1). Some advantages of solubility parameter use are provided by its correlation with other properties of solute and solvent (2, 3). Applications include such areas as paints and polymer formulation, extraction, and surfactant selection. When applied to oil extraction, the solubility parameter concept permits conditions to be specified for the optimum extraction of the seed oil by a SCF as demonstrated by King (4). Calculation of solubility parameters has been extended to supercritical fluids (5, 6), and we currently are investigating whether the solubility parameter concept can be of predictive or correlative value in the supercritical fluid extraction of oilseeds and other agricultural materials. Unfortunately, vegetable oils do not easily lend themselves to solubility parameter calculation by conventional methods. Low vapor pressures for oils (7) make difficult, even at room temperature and atmospheric pressure, the determination of energies of vaporization on which calculation of the solubility parameter depends. Computation of the solubility parameter from tables and molecular structures of oil components (8, 9) must be viewed with caution when extrapolated to supercritical conditions.

While evaluation of actual solubility parameters of vegetable oils at high pressure and elevated temperature involves considerable difficulty, determination of solubility parameter differences between an oil or liquid and another component such as supercritical carbon dioxide, in a two-phase system, uses straight-forward

application of experimental data taken with relatively simple apparatus. A small, stirred autoclave can be used for mixing and sampling from both phases after separation and equilibration. Solubility parameter differences between the supercritical carbon dioxide and the liquid solute can then be calculated from composition of the two phases using an equation published by Fujishiro and Hildebrand (10). These experiments and calculations are reported here for three vegetable oils and four other liquids of relatively high hydrogen bonding propensity with SCF-CO₂ as the second component.

EXPERIMENTAL

The soybean oil selected was a refined, bleached and deodorized commercial oil. The castor oil was a cold-pressed product obtained from a local pharmacy. Jojoba oil had been extracted with supercritical carbon dioxide from nuts obtained from a commercial supplier. The glycerol, ethylene glycol and n-butanol were reagent grade chemicals. All were obtained from Fisher Chemical Co. Carbon dioxide used in these experiments was liquified UN2187 grade (Matheson Division, Searle Medical Products Inc.) furnished in tanks without dip tubes.

Our stirred reactor was a 300 cc Bench Scale Magne-Drive Packless Autoclave (Autoclave Engineers Inc., 2930 West 22nd Street, Erie, Pennsylvania 16512). The autoclave had two sampling ports which allowed sampling from both the upper and lower phases. The reactor was equipped with a gas dispersion impeller for mixing the resultant phases. Temperature of the system (52 C or 72 C) was maintained by thermostatically controlled external heating tapes placed on the head and jacket of the reactor. By use of this method we were able to control internal temperatures to within ± 0.5 C. Both external and internal reactor temperatures were measured with thermocouples. Pressure in the system was maintained with a 30,000 psi rated, two-stage, double-ended, electric motor-driven, diaphragm compressor (Model J46-13427, American Instrument Company, Division of Travenol Laboratories, Inc., 830 Georgia Avenue, Silver Springs, MD 20190).

Fifty ml of liquid was placed in the stirred reactor and carbon dioxide at supercritical temperature charged into the system until the desired pressure was obtained. All charges were mixed at 1,000 rpm for at least 10 min and allowed to settle for at least the same length of time before sampling. Use of longer agitation and settling times did not change results. At least three and frequently four or more samples of each phase were taken. Pressure drops less than 10% of total pressure during sampling were recorded. Results were not affected by these pressure drops because of the small change in supercritical fluid and liquid densities with pressure under measurement conditions. Normally, all samples of a phase (usually the top one) were taken

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before sampling the other. Where a different sampling order was followed, results were not changed.

Samples of 3.7 ml were taken from both upper and lower phases. The apparatus provided for isolating the samples in a section of tubing by means of valves. The isolated sample was drawn off into a weighed container which allowed the carbon dioxide to come to a standard temperature and pressure with subsequent venting into another part of the apparatus for volume measurement. After rinsing the sample tube with a volatile solvent, the liquid was recovered by solvent evaporation and weighed with an analytical balance. This simple method recovered all the isolated sample. Molar volumes of each of the components as well as mole fractions and volume fractions in each of the phases were computed from weight, density and molecular weight. Average molecular weight of soy and jojoba oils was calculated from an analysis of oil composition.

Solubility parameter differences were computed from Equation 1, which has been used for calculation of solubility parameter differences between immiscible liquids (10), assuming the validity of the regular solution concept.

$$(\delta_1 - \delta_2)^2 = \frac{RT}{2} \left(\frac{1}{V_1} \ln \frac{X_{1B}}{X_{1A}} + \frac{1}{V_2} \ln \frac{X_{2A}}{X_{2B}} \right) / (\phi_{1B} - \phi_{1A}) \quad [1]$$

where δ is the solubility parameter, X the mole fraction, ϕ the volume fraction, T absolute temperature and V the molecular volume. R is the gas constant. In Equation 1, subscripts 1 and 2 refer to components and A and B to phases. In our experiments we selected the supercritical carbon dioxide as component 1 and phase A as the upper phase.

TABLE 1

Mole Fraction of the Liquid Component in Each Phase

Liquid		Pressures (psi)				
		5,000	8,000	10,000	16,000	20,300
Soy oil	X _{2A}	.08178	.04867	.04556	.0112	.03393
	X _{2B}	.00068	.00398	.01495	.03749	.03423
Jojoba oil	X _{2A}	.09344	.0092	.01028		
	X _{2B}	.00174	.0885	.07516		
Castor oil	X _{2A}	.0933	.0707	.05553		
	X _{2B}	.00032	.00112	.00110		
Glycerol	X _{2A}	.0079	.0056	.00975		
	X _{2B}	.761	.751	.830		
Ethylene glycol	X _{2A}	.78589	.78948	.56623		
	X _{2B}	.07338	.02227	.00846		
Triethylene glycol	X _{2A}	.38274	.27495	.24987		
	X _{2B}	.00078	.00129	.00636		
n Butanol	X _{2A}	.20226	.16222	.13619		
	X _{2B}	.14446	.174124	.14397		

Note: Each system was assumed to consist of two phases. The liquid was designated component 2 in each phase. The upper phase was designated A.

RESULTS

Tables 1 and 2 compare each of the phases at the temperatures used in our experiments. Mole fractions of the liquid component (component 2) are listed in Table 1. Volume fraction of component 1 (supercritical carbon dioxide) is given in Table 2. Absolute values for solubility parameter differences, $\delta_{CO_2-\delta_{liq}}$, are given in Table 3. Values were computed for system pressures of 5,000, 8,000 and 10,000 psi for all liquids and also at 16,000 and 20,300 psi for soybean oil.

For the series of hydrogen-bonding liquids, solubility parameter differences were estimated at 52 C, a convenient temperature for operation of the stirred reactor. Because we wanted to compare data for the oils with results from other experiments, measurements were taken at 71 to 72 C, although control of temperature at this level was more difficult than at 52 C. Standard deviation for calculated values of $\delta_{CO_2-\delta_{liq}}$ from the same charge was $\pm .23 \text{ cal}^{1/2} \text{ cm}^{-3/2}$.

DISCUSSION

Initial attempts to measure quantitatively the solubility of vegetable oils in supercritical carbon dioxide with a Jurgeson Gage (Jurgeson Gage and Valve Co., Burlington, Maine) designed for pressures up to 10,000 psi were not successful because of a tendency for droplets to form in the apparatus. The gage, however, did provide an opportunity to observe when two clear phases were present. Use of the stirred autoclave to estimate solubility parameter differences requires incomplete miscibility and relatively rapid attainment of equilibrium. Miscibility can be checked with the Jurgeson Gage, and equilibrium is more rapidly attained in supercritical fluid-liquid than in liquid-liquid systems.

TABLE 2

Volume Fraction of Supercritical Carbon Dioxide in Each Phase

Liquid		Pressure (psi)				
		5,000	8,000	10,000	16,000	20,300
Soy oil	ϕ_{1A}	.38713	.48004	.49902	.79529	.54657
	ϕ_{1B}	.98787	.92326	.75961	.52960	.54404
Jojoba oil	ϕ_{1A}	.42515	.87844	.85521		
	ϕ_{1B}	.97762	.40866	.43196		
Castor oil	ϕ_{1A}	.33282	.37790	.44146		
	ϕ_{1B}	.99360	.97626	.97698		
Glycerol	ϕ_{1A}	.98833	.99098	.98360		
	ϕ_{1B}	.17503	.16957	.10864		
Ethylene glycol	ϕ_{1A}	.18099	.17777	.37380		
	ϕ_{1B}	.91190	.97268	.98916		
Triethylene glycol	ϕ_{1A}	.37958	.47612	.49548		
	ϕ_{1B}	.99791	.99621	.98115		
n Butanol	ϕ_{1A}	.68183	.71885	.75133		
	ϕ_{1B}	.76291	.70125	.73942		

Note: Each system was assumed to consist of two phases (A and B). The liquid was designated component 2 in each phase.

TABLE 3

Absolute Values^a for Solubility Parameter Differences, $\delta_{\text{CO}_2}^{\text{liq}}$, Between Supercritical Carbon Dioxide and Liquid

Liquid	Pressures (psi)				
	5,000	8,000	10,000	16,000	20,300
Soy oil ^b	1.9	1.7	1.6	1.6	1.6
Johoba oil ^b	2.1	1.9	1.9		
Castor oil ^b	2.0	1.8	1.8		
Glycerol ^c	6.0	6.2	6.1		
Ethylene glycol ^c	5.7	6.3	6.7		
Triethylene glycol ^c	5.4	5.4	5.1		
n Butanol ^c	4.5	4.5	4.6		

^aSolubility parameter differences in $\text{cal}^{1/2}\text{cm}^{-3/2}$.

^bOil solubilities were measured at 71-72 C.

^cPolar liquid solubilities were measured at 52 C.

For most of the liquids shown in Table 1 solubility parameter differences were calculated assuming the liquids to be incompressible, i.e. that molecular volumes did not change with pressure, but where information was available, theoretical (11) or actual (12) compressibilities were also used. Comparison of results indicated that errors arising from neglect of liquid compressibility were less than experimental ones. Trial calculations assuming reasonable experimental errors in determined quantities of carbon dioxide and liquid in each phase also failed to produce large differences in computed results. The small change in solubility parameter difference resulting from large changes in pressure correlates with the shape of the solubility parameter vs pressure curve (5), as shown in Figure 1, and the small change in parameter value with measured pressure on the liquid. Larger differences between solubility parameters of the hydrogen bonding liquids and supercritical carbon dioxide than between oils and the same supercritical fluid also agree with the experience that super-

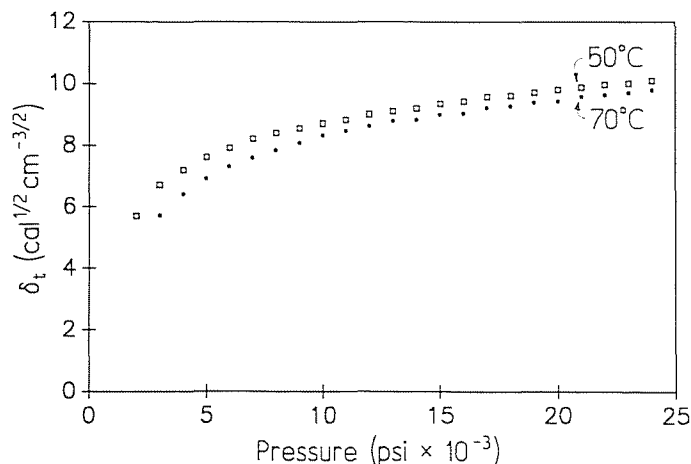


FIG. 1. Solubility parameter for supercritical carbon dioxide (5). Computed from $\delta_t = 1.25 P_c^{1/2} [P_r/2.66]$. □, 50 C; •, 70 C.

critical carbon dioxide acts much like a nonpolar solvent, such as hexane, in vegetable oil extractions.

Employment of liquid solubility parameters has proved of value in solving practical problems (13, 14). Computed values for solubility parameters of supercritical fluids correlate well with those expected when compared to liquids with similar molecular properties (5). Since the final result of our estimate is an absolute value of the difference, we cannot tell from this calculation which parameter has the higher value. Judgment concerning actual magnitudes of the two solubility parameters frequently can be made from estimates for supercritical fluid and from measured values for liquids under conventional conditions. For example, the solubility parameter of supercritical carbon dioxide can be computed from Equation 2, which was proposed by Giddings et al. (5) for dense gases:

$$\delta_{\text{gas}} = 1.25 P_c^{1/2} (q_r/2.66) \quad [2]$$

where δ_{gas} is the solubility parameter of the supercritical fluid, P_c its critical pressure, q_r is the reduced density of the gas and 2.66 is a constant which is equivalent to an average reduced density for the corresponding liquid. Computed from Equation 2 the solubility parameter of carbon dioxide at 52 C and 8,000 psi is about $8.5 \text{ cal}^{1/2} \text{ cm}^{-3/2}$.

For each of the hydrogen bonding liquids used in our experiment a range of solubility parameters values can be found in the literature (15 - 18). Parameter values at 52 C can be estimated from those at 25 C by means of Equation 3 (19).

$$\frac{\delta_2}{\delta_1} = \frac{1 - \text{Tr}_2}{1 - \text{Tr}_1} \quad [3]$$

where $\text{Tr}_2 = T_2/T_c$, and $\text{Tr}_1 = T_1/T_c$. T_c is the critical temperature.

Both the range of parameter values found in the literature for our hydrogen bonding liquids and the average value within this range are given in Table 4. If average values from this table are used, calculated solubility parameter differences between the liquid and supercritical carbon dioxide solubility parameters at 8,000 psi are 8.57, 7.08, 4.05 and $2.39 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for glycerol, ethylene glycol, triethylene glycol and n-butyl alcohol, respectively. Experimental solubility parameter differences for these conditions computed with Equation 1 from our data and listed in Table 3 are 6.2, 6.3, 5.4 and $4.5 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for these liquids in the same order. This is very satisfying agreement.

Within experimental error there is reasonable correspondence between solubility parameter differences expected from literature and those computed from stirred-autoclave data with Equation 1 for the four hydrogen bonding liquids. Solubility parameter difference values determined correlate with the observed relatively low solubility. Lower solubility parameter difference values for the oils reflect their higher solubility in SCF- CO_2 .

Inspection of Equation 1, however, shows that the amount of material, in terms of mole fraction, dissolved in each of the phases would depend upon more than just the overall solubility parameter difference. Molar

VEGETABLE OIL SOLUBILITY PARAMETER DIFFERENCES

TABLE 4

Solubility Parameters and Range of Published^a Values Computed at 52 C^b

Liquid	Solubility parameter range (cal ^{1/2} cm ^{-3/2})	Average value (cal ^{1/2} cm ^{-3/2})
Glycerol	17.56 - 16.16	17.07
Ethylene glycol	16.60 - 14.22	15.58
Triethylene glycol	13.91 - 10.47	12.55
n Butyl alcohol	10.98 - 10.70	10.89

^aPublished values in references 14 - 17.^bComputed from values at 25° using equation 2.

volume and volume fraction each have an effect. Figure 2 shows solubility of soybean and castor oils at several pressures. Although solubility parameter differences compared to supercritical carbon dioxide are similar for the oils, the weight percent dissolved in the carbon dioxide rich phase is considerably different. Some of the recorded difference can be attributed to average molecular weight. Also, although these oils are usually considered of low polarity and degree of hydrogen bonding, the extent of hydrogen bonding has been shown to be higher for castor than for many other vegetable oils (17).

Calculated absolute values of solubility parameter difference between supercritical carbon dioxide and the series of polar liquids used in our experiment agree well enough with values taken or computed from literature to indicate that data from a stirred autoclave can provide a useful estimate of these parameters. With sufficient attention to control of temperature, pressure and attainment of equilibrium conditions, results are reproducible and the calculation is not unduly sensitive to small environmental variations. By using the experimentally determined parameter difference along with computed parameters for supercritical carbon dioxide, one can estimate solubility parameters for vegetable oils under high pressures.

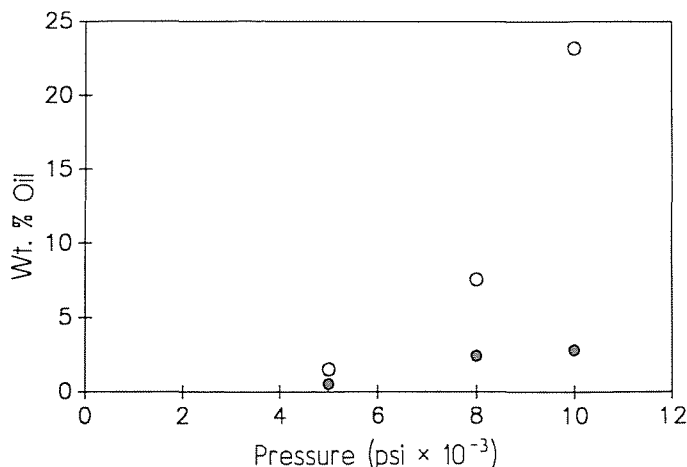


FIG. 2. Effect of pressure on solubility of oils in supercritical carbon dioxide (% oil in carbon dioxide rich phase). O, Soybean oil; •, castor oil.

Although parameter differences computed using the equation of Fujishiro and Hildebrand compare reasonably well with differences taken from literature, results in liquid-supercritical fluid systems should be interpreted with caution. Similar difference values can give considerable variation in percent solubility by weight. These variations can occur not only because of differences in molecular weight and molar volume, but also because of failure of "regular solution theory" to take into account such factors as hydrogen bonding and entropic effects which may be present in solution.

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